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GEOTHERMAL FIELD

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STUDIES OF SCALE FORMATION AND SCALE INHIBITORS
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INTRODUCTION

Interest in utilizing the geothermal resources of the Imperial Valley in California for the generation of electricity has accelerated rapidly in recent years. One resource in particular, the Salton Sea Geothermal Field, is attractive because of its high temperature and size. Recent estimates (1) of its potential for electrical power generation range between 1300 and 8700 MW per year (over a 20-year period). The fluid of this resource, however, is a high-salinity brine that is highly corrosive, and it contains several constituents that form deposits of scale on plant structures as the brine is cooled. Economical utilization of Salton Sea Geothermal Field will require techniques for controlling scaling and corrosion at acceptable levels.

Since 1974, the Lawrence Livermore Laboratory has been investigating various aspects of the technology for harnessing the energy of the Salton Sea Geothermal Field, and by 1976 it had been established (2,3) that acidification of the brine was an effective method for decreasing the rate of scale formation from hypersaline brine. However, this approach is costly both in terms of the chemical requirements and because it would necessitate using still more corrosion-resistant materials of construction. Moreover, alteration of the pH of the brine complicates the operation of equipment designed to process the spent brine for disposal into injection wells.

Thus, since late 1977, we have focussed our studies on the use of organic compounds as antiscalants (4,5). This approach is traditional in many other areas of industrial water treatment (6), but we found at the outset of our investigations that none of the proprietary additives that represented the state of art in 1978 were effective in controlling the scales formed from hypersaline brine.

The deposits with which we are dealing are unusual even among those of geothermal origin; they range in composition from primarily heavy-metal sulfides at wellhead temperatures ($\sim$200°C) to nearly "pure" amorphous silica at the temperatures of the effluent brine ($\sim$100°C). The highly siliceous scales represent the greatest problem because they can accumulate at rates as high as 3 mm/day. In view of the nature of the deposits, the high salinity of the brine, and the high temperatures involved, it is not too surprising that the conventional fluid treatment chemicals have failed as antiscalants. However, we have made some progress in identifying classes of organic compounds that will inhibit silica precipitation and scaling, and some of these results have been reported previously (5).

In the present paper we describe and review some additional results of our evaluation of organic compounds for scale control. Because of the unusual nature of the hypersaline brine, its deposits, and methods of handling, we also discuss in detail some aspects of the brine chemistry, scale composition, and our techniques for screening the candidate additives.

COMPOSITION OF BRINES OF THE SALTON
SEA GEOTHERMAL FIELD

Like many natural waters, the chemical compositions of geothermal fluids vary considerably, depending on a number of factors. These include the location of the resource, the location and depth of the well within the resource, and the flow rate of the well. Good summaries of the compositions of the major geothermal waters of the world have recently appeared in the literature (7,8).

At the wellhead, most geothermal fluids consist of a two-phase mixture of brine and steam; the exact composition of the brine phase depends on the method of flashing and it changes from stage to stage in a geothermal brine processing system. Sampling and chemically analyzing such fluids accurately are very difficult problems themselves (9). To completely characterize a wellbore fluid, for example, separate

analyses of the steam (gas) phase and the brine (liquid) are required together
with a measurement of the fraction of each phase. Because of the quite variable
composition of geothermal brines, the deposits or scales formed from them also
vary widely (10). Thus a brine treatment technique recommended for a particular
geothermal system or resource may not be effective for another. Even within a
particular brine processing plant, such as those at the Salton Sea Geothermal
Field, as mentioned above, the compositions of the deposits will vary from stage
to stage, and a single treatment technique may not be effective in retarding
deposits throughout the plant.

Geothermal resources have been classified according to four levels of temper-
ature and four levels of salinity (8). The Salton Sea Geothermal Field is among
the few in which the brines have both a high temperature (>240°C) and high salinity
(total dissolved solids >100,000 ppm). Like most of the high temperature
resources, these brines also contain high concentrations of silica (>400 ppm); this
corresponds to a condition of supersaturation at the lower brine flashing temper-
atures and is the source of the siliceous scales that are formed. Another general
distinguishing feature of the brines of the Salton Sea Geothermal Field, which also
influences the type of scales that are formed, is their slight acidity (pH 4-7).

All of the brine treatment studies conducted by the Lawrence Livermore
Laboratory have been done using two wells, Magmamax No. 1 and Woolsey No. 1, which
are owned and operated by the Imperial Magma Company. They are located in the
Salton Sea Geothermal Field, about 2 km south of the Salton Sea. Some typical
characteristics of Magmamax No. 1 are listed in Table 1; the values of the para-
meters listed are those found for brine that has passed through several flash
stages to reach atmospheric pressure and the boiling point at that pressure.
In this case, because of steam loss, this spent or effluent brine is ~20% more
concentrated in the nonvolatile salts than is the corresponding wellhead brine (11).
The effluent brine is less concentrated in volatile compounds; at the wellhead the
brine contains 1-2% CO_2, 30-60 mg/kg NH_3, and 10-30 mg/kg H_2S (12), and almost all
of these are lost by the time the brine reaches the effluent temperature. Some
boron and mercury are also lost to the steam phase. The net effect of the loss of
volatiles, especially CO_2, is a rise in pH of the brine.

As can be seen from the data in Table 1, the brine is primarily a solution of sodium, potassium, and calcium chlorides, and it has an interesting array of minor constituents that are very important in the formation of scale. Brine obtained at the wellhead is virtually oxygen free, and is reducing in character as reflected by the presence of the high concentrations of hydrogen sulfide. After flashing to atmospheric pressure and loss of hydrogen sulfide, the Eh of the brine has been found to be +0.20 V vs. S.H.E. (13). This potential is probably determined by the Fe^{3+}/Fe^{2+} couple, with Fe^{2+} chloride complexes being the predominant species. All of the other elemental species are also presumably in their lowest ionic oxidation states. On the other hand, some sulfate is always found in these brines; it is not known whether it is in equilibrium with the sulfide or hydrogen sulfide downwell, or whether it is acquired during flow of the brine through the reservoir formation. In Woolsey No. 1 brine, the concentration of sulfate is ∿90 mg/kg.

GENERAL CHARACTERISTICS OF SCALES OF
SALTON SEA GEOTHERMAL FIELD

Evaporative concentration and cooling of depressurized brine from the Salton Sea Geothermal Field results in a rapid deposition of scale on surfaces exposed to brine. The general characteristics of these scales as determined by various investigators at this resource are summarized in Table 2. The notable feature, as mentioned above, is the trend from a metal sulfide assemblage at high temperatures to a nearly pure amorphous silica scale at the lowest temperatures. Skinner et al (15), on analyzing scale from Well IID No. 1, found several sulfide minerals which have not been found in the Magmamax No. 1 scales on examination at this Laboratory (14), but which were predicted in computer code calculations (16). The sulfides precipitate because of the cooling of the brine and the pH rise that accompanies the loss of CO_2 (16,17).

Another important trend is the increase in scaling rate as the temperature of deposition decreases and as the proportion of amorphous silica increases. The reservoir brine, upon cooling at the surface, becomes supersaturated with respect to the equilibrium solubility of amorphous silica; silica thus precipitates at a rapid rate that is enhanced by the pH rise upon flashing. The iron compound or

compounds that are always present in the predominantly silica scales (to the extent of 1-5% as Fe) have never been positively identified, but they may be important in the mechanism of the nucleation of the scale. Montmorillonite clay and magnetite (Fe_3O_4) have been found where there was extensive corrosion of the substrates, but these may not be the compounds generally present in the silica matrix.

Obviously, the most pressing task in the scheme of scale retardation at the Salton Sea Geothermal Field is to retard the formation of the siliceous scale, because it forms at the highest rate. Moreover, there is considerable evidence (14) that sulfides rarely, if ever, form directly on a scaling substrate and that the silica matrix is the "glue" that holds even the high temperature scale together. Thus the control of the precipitation and deposition of silica from hypersaline geothermal brine may be the key to scale control at all temperatures.

MECHANISM OF FORMATION OF SILICA SCALE

Like other types of scale deposition, the formation of silica scale in geo-thermal systems is a complex process involving kinetic, thermodynamic, and fluid dynamic factors (18). Silica scale deposition, however, is unusual in that an amorphous, rather than crystalline deposit is formed, and the process by which silica precipitates to form scale has some unique features. Several groups of investigators have recently published the results of laboratory studies and reviews of silica precipitation and scaling (19-26), and these findings have shed new light on the subject. There is also a voluminous older literature dealing with this aspect of silica chemistry.

Silica exists in true solution as a monomer in equilibrium as dissociated silicic acid:

$$SiOH_4 \rightleftharpoons SiO(OH)_3^- + H^+$$
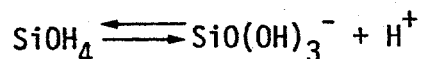
In a supersaturated solution, these species undergo polymerization reactions by a mechanism and a rate that depend on the pH of the solution (19) and the degree of supersaturation (the ratio of the concentration to the equilibrium solubility). The polysilicic acids thus formed, e.g.,

```
      OH   OH   OH
      |    |    |
   HO-Si-O-Si-O-Si-OH
      |    |    |
      OH   O    OH
           |
        HO-Si-OH
           |
           OH
```
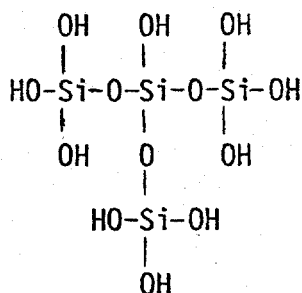
continue to polymerize until colloidal-size nuclei are formed or deposition of scale commences. A diagram representing the entire process is given in Figure 1. Two major pathways for the deposition of scale can be distinguished: homogeneous nucleation in which colloidal particles are formed in the bulk of the fluid (these particles then aggregate and become attached to a substrate); or heterogeneous nucleation, in which nuclei are formed directly on the substrate surface. In the latter process, continued growth can occur by direct deposition of monomeric or polymeric species (21,23). From the pH dependence of the overall rate of the disappearance of monomer, it appears that the maximum rate occurs at a pH where there are equal concentrations of the neutral $Si(OH)_4$ and ionic $SiO(OH)_3^-$ species (26).

Both the rate of formation and morphology of silica scale depend on the mode by which the scale is formed. At a supersaturation ratio of 2 to 3 or higher, homogeneous nucleation is favored (20,21), silica rapidly precipitates, the lineal growth of scale is largest, and the scale has a generally soft texture. This scale is also most likely to occlude portions of the liquid phase. At lower supersaturation ratios, there are increasingly long induction periods before silica polymerization can be detected (20,21,24,25), more of the growth of the scale occurs directly from monomeric species (21), and an increasingly dense, vitreous scale is formed at a slower rate.

APPROACHES TO THE CONTROL OF SILICEOUS SCALE

Several methods for controlling the formation of geothermal siliceous scale have been proposed and tested with varying degrees of success. These techniques may be summarized as follows:

1. <u>Brine pH Reduction</u>. Acidification of the brine to a pH of 3-4 has been tested by Owen and coworkers (2,3,17) in the Imperial Valley and by Rothbaum et al, in New Zealand and has proved to be effective. It is based on the decrease in the rate of silica polymerization with pH (17,19), the suppression of the precipitation of the metal sulfides at lower pH, and the prevention of the adherence of corrosion products to steel surfaces. Disadvantages in this approach are the high cost of the acid (∿300 ppm are required), the increased corrosion rates resulting from the lowered pH, and the need for pH control equipment.

2. <u>Brine pH Increase</u>. The philosophy of this approach is to accelerate homogeneous nucleation to the point where homogeneous precipitation will be more likely than heterogeneous deposition. This technique is proposed in a patent by Wilkins (27), but to the author's knowledge, it has not been thoroughly tested. Implementation would appear to require a delicate adjustment of the residence times of the brine in various portions of a geothermal flash system, and would require special equipment to handle brine with high solids levels.

3. <u>Sludge Seeding</u>. In this method, seed material in the form of finely-divided silica solids would be added to the brine, which would promote the precipitation of silica from the brine. A high ratio of the surface area of the seed particles to the area of the exposed brine-handling equipment would be required, as well as a rapid lowering of the silica supersaturation ratio. This principle has proved to be useful in the design of reactor-clarifiers for geothermal effluent brine (28), where dissolved silica is reduced to near equilibrium levels, and where the precipitated silica is continuously recycled as a sludge. As a method of silica scale control, it has also appeared promising in experiments

at our facility (29) and that of the Imperial Magma Company (30). This technique also requires the use of equipment that will tolerate very high levels of suspended solids in the brine.

4. <u>Treatment with Chelating Agents</u>. Treatment of the brine with complexing agents to combine with the scale-forming species (6) probably has little practical value for the Salton Sea geothermal brines because stoichiometric amounts of the complexing agents are required and the species to be complexed are present at high concentrations. In the case of silica, however, we did briefly attempt to form the silicomolybdate complex on-stream in hypersaline brine with the hope of inhibiting silica precipitation and scaling, but there was apparently no reaction (31). Such brine constituents as Ca^{2+} and Fe^{2+} may play a role in the formation of silica scale (25), but their concentrations also are too high to be controlled economically by chelation techniques.

5. <u>Scale Adhesion Inhibitors</u>. This approach to scale control involves the use of additives that adsorb on the scale-forming particles or the scaling substrate, or both, to prevent the adherence of the scale on the substrate. Such agents could be used at concentrations stoichiometrically less than those of the scale-forming reactants, since they depend on surface adsorption for their action. An example of this type of inhibitor are the filming amines used in corrosion inhibition, which strongly adsorb on metal surfaces. A test of an additive of this type in our studies (29) revealed that the hardness and adhesion of the 125°C scale was reduced, but not the quantity of adhering scale.

A somewhat similar approach, developed by R. W. Erwin (32), is to coat the surfaces of the brine handling apparatus with a hydrophobic layer, thus rendering the accumulated scale, which is composed principally of hydrophilic silica, less adherent. Using an additive mixture based on cottonseed and other oils, Erwin has tested this technique at the Cerro Prieto, Mexico, and Brawley Geothermal Fields with some promising results (32). Our evaluation of the process by means of a short-duration test (33) indicated that the siliceous scale was indeed significantly less adherent where fluid velocities were high and macroscopic eddies were

absent, such as in straight runs of pipe. Elsewhere, scale accumulated at a greater rate than when exposed to untreated brine, and the scale incorporated large quantities of the oil additive. A key feature of scale adhesion inhibitors in general, which may limit their usefulness when used alone, is that they do little to arrest the nucleation and/or growth of particles from the scale-forming reactants.

6. Treatment with Anti-Precipitants. This technique of scale control involves the use, at low, substoichiometric concentrations, of chemical agents that decrease the rate of the scale-forming reactions by adsorption on the surfaces of the nucleated particles of the scale compound or the deposit itself. Depending on their function, these agents are also known variously in the literature as dispersants, threshold inhibitors, and crystal distorting agents. The latter retard the formation of scale by interfering with the normal crystal growth patterns of the scale-forming compounds. Similar inhibition of amorphous scales can be obtained, in principle, by adsorption of inhibitor compounds on the colloidal particles that aggregate to form scale. The basis for this type of inhibition is described in colloid stability theory.

There are two general mechanisms whereby colloid stability is imparted: electrostatic stabilization and steric stabilization (34,35). (Note that these same principles are also invoked when the goal is a deliberate destabilization or flocculation of a colloid, such as in water treatment for the removal of solids.) In the case of electrostatic stabilization, the stabilizing agent or medium causes the colloidal particles to acquire sufficient surface charge to repel one another and remain in suspension. Steric stabilization involves the adsorption of the inhibitor (usually large polymeric molecules) on the colloidal particles so that the resulting configuration interferes with the close approach and subsequent aggregation of the particles.

Compared to the other potential methods of scale control, the use of colloid stabilizers, i.e., substances that actually retard the flocculation of the suspended solids at an early stage (sizes <0.1 μm) offers several advantages. Small, economical amounts of inhibitor could be used, and the

suspended solids levels in the fluid would be inherently low. Compared to acidification, corrosion rates of materials would not be as high; however, the unscaled surfaces still would be expected to corrode more rapidly than those that are scaled and partially protected.

It is evident that the conditions existing in the processing of high-salinity geothermal brines are quite different from those of the usual waste or even boiler water treatments. Nevertheless, the use of colloid stabilizing and crystal distorting agents have shown promise in geothermal applications. For the inhibition of calcite scales formed from the low-salinity brines of the East Mesa, Imperial Valley, Geothermal Field, Vetter and Campbell (36) have recently shown that 1 ppm of a phosphonate-type inhibitor was very effective. The work we describe here is based on attempting to find an effective stabilizer for colloidal silica in high-salinity geothermal brines.

Although we have found a number of compounds that do retard silica precipitation and to some extent scaling (4,5,29,31,37,38), there is yet no direct evidence of whether the mechanism of stabilization is actually electrostatic or steric. However, it is probable that steric effects are the more important ones, because of the pronounced compression of the electrical double layer surrounding the particles in the hypersaline brine (34,39). Using the formula of Napper (34), the thickness of the double layer in Magmamax No. 1 brine (see Table 1; ionic strength = 5.2) is calculated to be 1.5 Å, much less than the dimensions of most adsorbing molecules. On the other hand, the colloidal silica is probably negatively charged due to the ionization of the silanol groups (19), and this may play a role in which compounds are most strongly adsorbed. The very high ionic strength of the brine also has the effect of reducing the overall dimensions of polymer chains in solution (40), causing them to coil inward on themselves, and this may have an effect on how they are adsorbed on the silica particles.

CHARACTERISTICS OF AN IDEAL ANTISCALANT
FOR GEOTHERMAL BRINE

Chemical additives for scale control in geothermal systems are required to meet a number of specifications, some of which are unusual in the field of water treatment technology. These desirable characteristics can be briefly outlined as follows.

1. Type of Antiscalant. As discussed above, the best type of antiscalant in theory is one that inhibits particle nucleation and/or growth -- preferably indefinitely. Such an inhibitor would not only prevent the growth of scale, but also prevent an increase in the level of suspended solids in the brine. High levels of suspended solids complicate the handling of the brine in plant equipment, and even low levels (a few ppm) interfere with the disposal of the spent brine in injection wells (28,41). However, it is likely that the successful antiscalant additive will be a mixture of compounds, each having a different functionality. For example, an antiprecipitant could be combined with a scale adhesion inhibitor or perhaps a corrosion inhibitor; and mixtures of compounds specific for several scale-forming compounds might be used.

2. Thermal Stability and Solubility. The high fluid temperatures that are encountered, especially at the Salton Sea Geothermal Field, place stringent requirements on the thermal stability of candidate additives. However, in most geothermal systems, fluid flow velocities are high, and the residence times of the brine in the various portions of the plant are usually only a few minutes, so that an additive injected at the high-temperature, front end of the plant would usually be exposed to the high temperature for only a short time. Another potential problem is a limited solubility of the additive in the brine because of the high salt concentration, or because of an inverse solubility/temperature characteristic. In our testing of additives, we have found several compounds, some of which are good silica precipitation inhibitors (37), that precipitated from the brine at 200°C and formed a scale deposit termed by Vetter "pseudo scale" (42). The additive obviously should also not react

with any of the otherwise inert constituents of the brine to form an insoluble substance. The precipitation of calcium by high concentrations of phosphonate inhibitors is an example of this problem (36).

3. Toxicity. Concern about the environmental impact of the use of scale-control additives depends to a large extent on the method of brine disposal. Even if 100% brine reinjection is employed, there may be temporary brine-holding ponds that could contaminate the local groundwaters. Consideration should also be given to the possible carryover of the additive in the steam phase or the vented non-condensable gases. Finally, if the additive does thermally decompose, it is possible for the fragments to be toxic.

4. Other Physical Characteristics. Aside from the possible formation of solids that could plug the pores of the injection well formation, the injectibility of the brine containing the dissolved additive is open to question and must be evaluated. High molecular weight polymers, even though completely soluble, are known to limit the passage of fluid through small pores (43). The additive should not cause the formation of a foam in the brine; in flashed-steam type facilities, such a foam could cause improper operation of the brine/steam separators. Because large quantities of a scale control additive would be used in a typical geothermal plant (see below), the concentration of the additive solution should be as high as possible so that solvent consumption is minimized.

5. Compatibility with Solids Removal Processes. Future utilization of the brines of the Salton Sea Geothermal Field may involve processing of the brine for solids removal prior to disposal (28,44), rather than direct reinjection. This involves the use of a reactor/clarifier in which the brine contacts a silica sludge to reduce the silica concentration to equilibrium levels. Most of the suspended solids are removed in this operation, and sand filtration is used to further purify the fluid for injection. If such processes are used, the impact of silica scale inhibitors on their operation should be assessed. The perfect silica precipitation inhibitor would obviate such solids removal equipment. For less-than-perfect inhibitors, methods may have to be devised to defeat their action in the reactor/clarifier.

6. <u>Cost of Additive</u>. Because such large quantities would be required, an overriding consideration in the use of chemical additives for geothermal scale control is the cost of the chemical itself. Assuming that 1 kWh could be generated from 50 kg of brine at the Salton Sea Geothermal Field (45), and the concentration of additive in the brine is 20 ppm, the quantity of additive required would be ∿900 kg/day for a typical 50 MW power plant. The concentration used places a constraint on the price of the additive. Assuming that the cost of power generation is ∿33 mill/kWh (45), at 20 ppm and $2.20/kg ($1.00/lb), the additive would represent 6% of the cost of power generation. The beneficial effects of a chemical additive treatment will always be measured against the alternative techniques of scale control, and since periodic plant cleaning will probably be required, brine treatments will be compared as to the frequency of cleaning that they entail. Moreover, the ease of removal of the scale as a result of brine treatment, as well as the simple degree of scale abatement, should be a consideration in evaluating a candidate additive.

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BRINE TREATMENT TEST FACILITY

Figure 2 is a schematic diagram of the apparatus we have used to test various methods of brine treatment at the Salton Sea Geothermal Field. In this facility two-phase fluid from the geothermal well is first passed through a centrifugal-type separator. The steam is discarded and single-phase brine is obtained at nearly well-head temperature and pressure. The brine is then divided into two nominally identical channels for testing of the additives. The brine in each channel is flashed to 125°C in flash vessels and then flows to an atmospheric receiver. The "delay stage" provides brine at atmospheric pressure, a temperature of 90-100°C, and aged ∿10 min. with respect to the 125°C flash.

Brine flow is maintained in each channel at 26 l/min. (7.0 gal/min.) by monitoring the pressure drop, 3.7 kPa, (15 in. H_2O) across an orifice plate that is cleaned periodically. Additive solution (at about 0.5-1.0% strength) is metered into the brine using high pressure pumps equipped with pulsation dampeners,

and this flow is monitored by means of turbine flow meters and maintained in the range of 50-150 ml/min. The additive solutions are introduced into the flowing brine through a concentric, 6-mm (1/4-in.) tube located 2.4-m upstream from the first test specimens. The accuracy of maintining a desired concentration of additive was determined in a tracer study using cesium ion and found to be ±10%.

TEST TECHNIQUES

Two basic approaches have been taken to studying the processes of scaling by the hypersaline brine and in searching for an organic additive that would minimize this scaling. First, candidate additives have been screened on the basis of their effect on the rate of precipitation of silica from samples of brine held at 90°C. If an additive appears to inhibit the precipitation of silica from homogeneous solution, the additive is then considered for evaluation of its effect on the scaling tendency of the brine. To conserve valuable field testing time, only the most promising additives are subjected to the scaling test.

In the precipitation test (46), the additives are injected into the brine at ∿210°C as described above, and the brine samples are collected for study from the 125°C sampling ports. During sampling, the brine flashes to 105°C. It is then placed in air-tight, Viton-gasketed, 130-ml, screw-cap glass bottles and incubated at 90°C. For incubations longer than 2 h, sealed glass ampoules are used (46). At appropriate intervals after sampling, the bottles are opened and the contents filtered through fine-porosity glass crucibles. The silica remaining in the filtrate is measured by atomic absorption spectrophotometry using the method of standard additions. Measurement of the silica in this manner has been shown to yield values for the total concentration of silica (monomeric, polymeric, and particulates <1 μm in size) not retained by the filter. The initial concentration of silica in the brine sampled at the effluent port is determined in samples immediately acidified with hydrochloric acid. The collected solids are dried in air at 105°C and weighed as a measure of the suspended solids concentration of the brine. Normally, lack of activity in the precipitation test is cause for rejection of the candidate additive. However, in our early tests with proprietary additives (29) sludge seeding (29), and the Austral-Erwin process (33), where activity as a precipitation inhibitor was not presupposed, scaling tests were conducted as the primary method of evaluation.

The scaling behavior of the brine is measured, as shown in Figure 2, by placement of specimens at three points in the system: at 210°C, 125°C, and in the brine from the delay stage at ∿90°C. At the two higher temperatures the following types of specimens are used:

2.5-cm (1-in.) i.d. sections of mild steel pipe

0.6-1 mm thick, flat coupons of three materials: AISI 1009 mild steel, Teflon TFE, and Hastelloy C-276

Perforated disks of type 304 stainless steel, through which the brine was flowed. The disks were contained in Millipore filter holders connected to sidestreams.

At 90°C, the specimens are short sections of 6- and 13-mm o.d. mild steel tubing. Coupons of three different materials are used to provide an indication of the effects of substrate corrosion on the scaling rates. Neither Teflon TFE (47) nor Hastelloy C-276 (13) are attacked at an appreciable rate by the hypersaline brine.

An indirect estimation of scaling rates is obtained by measurement of corrosion rates using Petrolite Instruments linear polarization resistance (LPR) equipment. Probes fitted with AISI 1018 steel electrodes are located (as shown in Figure 2) at the 210 and 125°C points in the system.

A major emphasis in our work has been to develop and use techniques of scaling rate measurement that would minimize the time required to evaluate a single additive or process, yet provide useful information for prediction of performance in larger facilities and for longer times. For accurate measurement of the scaling rates of the brine at 210 and 125°C, it has been found that exposure times of ∿3 days are required. The flat coupons of the three different materials have been the most reliable specimens, and their mounting configuration also reveals the effects of macroscopic turbulence in the flow streams. The perforated disks (which have 0.4-mm-diameter holes) reveal scaling tendencies in ∿24 h, but have not always been reliable because they are vulnerable to plugging by transient, high levels of particulates in the brine (33). At the effluent brine temperature of 90°C, the best indicators of scaling tendency are the tubing sections, which accumulate sufficient scale in 12-24 h for accurate measurement.

RESULTS OF MEASUREMENTS OF SCALE AND
SCALING RATES IN UNTREATED BRINE

The marked dependence of the characteristics of the geothermal scale on the temperature of deposition has already been noted. The rate of precipitation of silica and hence the scaling rates also vary significantly with the salinity of brine. In general, the higher the dissolved salt concentration, the higher the rate of scaling, which is due principally to the lowered equilibrium solubility of silica (11,20). This effect has been observed very clearly in our work with Magmamax No. 1 well, as illustrated in Figure 3. These data were obtained during measurements at different flow rates of the well,[*] which causes the salinity of the brine to vary. Increased well flow rates also increase the concentrations of silica slightly, and this enhances the effect. Such variations of scaling rate also occur at the other temperatures (31), and they require that comparisons of the effects of scale-control techniques be carefully made on an equal-salinity basis.

Also illustrated in Figure 3 are the changes in scaling rates as the substrate material is varied. It is apparent that with the relatively short exposure times employed, the inert materials accumulate scale at a lower overall rate. This is caused by the fact that the Teflon and Hastelloy surfaces lack the corrosion reactions, which, for the mild steel, provide a matrix for the initial adherence of the siliceous scale. There may also be a longer induction period before scale begins to deposit on the more inert surfaces. As the exposure times increase, or at fixed exposure time with more rapidly scaling brines, more of the scale growth occurs on a predominantly silica matrix, and the effects of the underlying metal or plastic are diminished as far as the overall rate of growth is concerned. However, differences still remain among substrate materials in the strength of adhesion of the scale layer (47). The slightly greater rate of growth (and adhesion) of scale on TFE Teflon compared to Hastelloy results from its greater surface roughness, partly brought about by the development of fibrils on the surface of the Teflon exposed to the high temperatures (47).

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[*]The brine-treatment system flow rates are held constant.

The interactions of the corrosion reactions of mild steel with the "purely scaling" reactions of the brine, when the steel is first exposed to the brine, have been examined in detail by various microscopic surface analysis techniques (48). Some interesting findings have emerged, but not all of the picture is clear. Two effects of the corrosion of the iron are hypothesized to influence the deposition of certain constituents from the brine. One is the local rise in pH that accompanies the dissolution of the iron, and the other is a direct replacement of iron by some of the more noble constituents of the brine such as copper, lead, and silver. In many instances, metallic lead and silver have been found incorporated into the scales, and microprobe analysis frequently demonstrates considerable heterogeneity. The effect of the corrosion reactions on the composition of the scale is reflected in the differences in the scales formed on different substrates. This is illustrated in Table 3, which lists the results of a bulk analysis of scale by the x-ray fluorescence technique. Corrosion of the steel causes the proportion of scale that is silica to be decreased and enriches the scale in copper, antimony, arsenic, and sulfur, as well as iron. The specific compounds present have not been identified, but the effect is rather dramatic in view of the very low concentrations of some of these elements in the brine (see Table 1). These differences in scale composition again are due merely to the relatively thin layers that are analyzed -- thick (several cm) layers of scale formed during longer exposures at the Salton Sea Geothermal Field under comparable conditions exhibit such enrichment of the minor constituents only near the substrate surfaces and this does not significantly contribute to the bulk analysis.

These variations in the rates of formation and composition of the scales with temperature, brine salinity, and substrate material are important considerations in the testing of scale control agents, particularly when techniques involving short term exposures are used.

RESULTS OF TESTS OF ORGANIC SCALE INHIBITORS

Thus far, in our testing, over 75 compounds representing a number of different classes of organic substances have been examined for their effect on silica in hypersaline geothermal brine (4,5,29,31,37,38). The most active compounds fall into two general classes: substances that are highly substituted in the oxyethylene moiety, $-CH_2CH_2O-$, and those with strong cationic character derived from nitrogen. Table 4 lists a number of the types and examples of compounds that have been found to inhibit the precipitation of silica from hypersaline brine. It is notable that the anionic-type compounds such as the acrylates, sulfonates, and phosphonates have consistently shown little activity toward silica in this brine.

Two of the most powerful inhibitors that have been discovered are the Ethoquad 18/25, which has both oxyethylene substitution and strong cationic character, and the cationic polymer, PAE·HCl. The results of a test of these compounds as silica precipitation inhibitors are shown in Figure 4. In this test, the Ethoquad was combined with Dequest 2060. This compound is a Monsanto phosphonate inhibitor for calcium carbonate (36); it has no direct activity toward silica, but as described below, it was tested in combination with the Ethoquad as a scale inhibitor. As shown in Figure 4, untreated brine under these conditions precipitates silica so rapidly that, in 15 min., the level of suspended solids reaches 250 mg/kg and the dissolved silica drops to 50% of its initial value. The Ethoquad, and to a greater extent, the PAE·HCl are effective in maintaining the silica in solution or in suspension as small submicron particles.

The mechanism of this inhbition is only speculative, but it is probable that it involves adsorption of the inhibitor compound on the surface of the silica particles to sterically stabilize the colloidal solution (34,35). Thus the inhibitors do not inhibit the nucleation of the silica particles; rather, they retard the aggregation or flocculation of the particles after nucleation. In the case of the polyoxyethylene compounds, hydrogen bonding between the silanol groups and the oxygens or terminal hydroxyls (49) may be the mode of adsorption. Cationic surfactants have been reported to adsorb on silica mineral surfaces through an ion-exchange mechanism (50), and that may be operative here. The silica particles are probably negatively charged because of the partial ionization of the silanol

groups, and this may lead to enhanced interaction with the cationic inhibitors. In any event, it appears that the ideal molecule for application here would be one that anchors itself tightly to the surface of the colloidal particles, presents a hydrophilic moiety to the aqueous medium, and is a certain minimum molecular size to produce steric repulsion.

There is some evidence that the optimum size molecule is in the neighborhood of a molecular weight of ~10,000. An investigation of the effect of molecular weight of the pure polyoxyethylenes (Union Carbide Carbowaxes and Polyoxes), the results of which are shown in Figure 5, revealed that the peak activity was at 14,000. However, the PAE·HCl that proved effective has a molecular weight of 120,000. Lower molecular weight versions of this polymer will be tested in future work. For each type of compound, activity as an inhibitor may be confined to a fairly narrow size range. Small molecules would produce weak steric stabilization, while large molecules or long polymer chains are likely to bridge between particles and enhance flocculation. In fact, cationic polymers similar to some of those we have tested are widely used in the water treatment industry as flocculants (6,51), and one had shown activity in experiments with the reactor-clarifier solids-removal process for this same geothermal brine (28).

The precipitation screening tests provide a good relative ranking of the activity of the candidate additives toward the silica in the geothermal brine under plant-type injection conditions. This manner of evaluation inherently tests the resistance of the compounds to the high temperature brine. However, the inhibition of the precipitation of silica in the bottled, stagnant solutions represents much milder conditions than exist in the flowing turbulent brine, which lead to the scaling of plant surfaces. The high rates of fluid shear enhance flocculation (52); and the impingement of the fluid on solid surfaces tends to enhance scale deposition -- although at very high fluid velocities, particle erosion may aid in keeping surfaces clean.

Several of the most promising precipitation inhibitors have been tested to determine their effect on the scaling tendency of the brine. All of the substances that retarded the homogeneous precipitaiton of silica at 90°C also decreased the growth of scale at 90°C, as measured by the tubing specimens installed after the delay stage. Those tested were Natrosol 250LR, Ethomeen C/25 and 18/60, Carbowax 14,000, Ethoquad 18/25, and a combination of Ethoquad 18/25 and Dequest 2060.

Carbowax 14,000 reduced the growth of scale at 90°C by ~70%; however it and the Ethomeen ethoxylated amines increased the rate of scaling at 125°C. Natrosol 250LR had no effect on the scale at 125°C.

The failure of Carbowax, Natrosol, and the Ethomeens to reduce the scaling at higher temperatures probably is a result of their diminished water solubility as the temperature is increased. The polyoxyethylene and cellulose derivatives characteristically have an inverse solubility/temperature behavior (40,53,54); their precipitation from solution takes place at a temperature known as the cloud point. The cloud point of solutions of these subtances is also lowered by in- creasing amounts of dissolved inorganic salts such as those found in the geothermal brines (54). Little work has been done in determining cloud points above 100°C, but it appears from data on a variety of nonionic surfactants (35,40,53,54) that the cloud points of the additives which we tested are in the range of 50 to somewhat greater than 100°C. Thus at the 125°C temperature, where much of our scaling rate measurements are made, there may not be enough of the additive in true solution to react with the colloidal silica. In the case of Natrosol 250LR, this may be the reason why very little scale abatement was observed. In the case of the Carbowax 14,000 and the Ethomeens, where there was apparently an increase in scaling rate at 125°C, the reduced solubility could have led to bridging of the polymers between particles and an enhancement of flocculation. Another possibility is that the precipitation of the additive itself could form a pseudo-scale by providing additional nuclei for precipitation of the silica.

Quaternary ammonium compounds that are ionic salts and acid salts of amines that are highly ionized theoretically have fewer high-temperature solubility limitations and greater compatibility with the geothermal brines. Thus our most recent testing has focussed on these classes of substances (31,38). At the lower temperatures, the performances of the Ethoquad 18/25 and the combination of Ethoquad with the calcite-scale inhibitor Dequest 2060 (diethylenetriamine pentamethylene phosphonic acid) were the best of the additives that we have tested thus far. The results of these scaling tests are summarized in Table 5.

The measurements of the scaling rate at 210°C show no decrease as a result of the additive treatment. No organic compound that we have tested has shown a beneficial effect at this temperature. In the case of the experiment with Ethoquad alone, the apparent increase in scaling rate at 210°C was due to an upset in the well flow that caused an abnormal influx of particulate matter, which lodged on the specimens at the first stage of the system (31).

At 125°C, the results indicate that the additives retard the formation of scale to a slight extent -- the degree being 15-44% depending on the substrate material. At this temperature there is no substantial difference between the Ethoquad and the Ethoquad/Dequest combination. Both additives changed the morphology of the scale: compared to the normal scale, the scales formed in the presence of the additives had a smaller particle size, a different macroscopic consistency, and were easier to remove from the specimens.

The additives were most effective at 90°C. With the Ethoquad alone, there was a 44% reduction in scaling rate and with the Ethoquad/Dequest mixture, the reduction was 81%. The results for the mixture are especially encouraging because it was tested under the highest salinity brine conditions. It also appears that the mixture of the two compounds is somewhat synergistic. The additives also slightly improved the ease of removal of the scale at this temperature.

The disappointingly low antiscalant activity exhibited by Ethoquad at 125 and 210°C cannot be attributed to a lack of solubility of the additive at these temperatures. A reasonable explanation is that the scale formed at these temperatures, compared to the scale at 90°C, grows to a greater extent from monomeric or small-molecule, polymeric silica rather than from the aggregation of sub-micron particles, and that this route cannot be inhibited by the additive. Adsorption of the additive may still take place on the scale deposit, but it probably would not interfere with the addition of small molecules. If this is the case, finding an additive that will dramatically inhibit the high-temperature silica scale by the classical steric stabilization mechanism may be impossible. The best hope may lie in either combinations of compounds of different functions, or pH adjustment to change the rate of nucleation, coupled with an organic precipitation inhibitor. Further work on these ideas is in progress.

When the performance of these additives is viewed over the whole temperature range, the degree of scale inhibition is still not very attractive economically, although the greatest abatement does occur where the scaling tendency of the brine is highest. The degree of scale inhibition achieved at 125 and 90°C is comparable to that found in longer-term tests of acidification at pH 4.5 (11). Acidification, however, is markedly superior at the higher temperatures.

Since our scale control investigations are continuing, the Ethoquad/Dequest additive represents only an interim recommendation. Further studies may reveal better inhibitors; e.g., the PAE·HCl has already been shown to be a more powerful antiprecipitant but has not yet been tested as an antiscalant. Other forms of this class of substances, quaternary ammonium compounds, and polyethylene imines will also be examined. Meanwhile, the Ethoquad or Ethoquad/Dequest mixture has several attractive characteristics in the criteria that were outlined above. These compounds have exhibited high temperature stability (36,38), are virtually non-toxic at the concentrations used in the brine, are available as concentrated liquids at a cost of $1-2 per pound, are low molecular weight compounds (500-1000), and are not strong enough as silica precipitation inhibitors to affect the removal of silica by sludge contact. These additives should also have potential application to other geothermal brines, particularly those where silica precipitation rates are lower because of lower salinity, lower degrees of silica supersaturation, or different temperature regimes. Critical factors in the action of the inhibitors will still be the pH of the brine and the particle growth history of the precipitating silica in the particular geothermal system.

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Table 1.   Typical characteristics of Magmamax No. 1 brine after flashing to
atmospheric pressure (105°C).

pH: 5.8

Density: 1.17 g/cm^3

Chloride concentration: 4.5 Mol/l [160,000 ppm(v)]

Total dissolved solids: 22%

Eh: +0.20 V vs SHE

Resistivity: 5.5 Ω-cm

Composition:

Element	Concentration, mg/kg	Element	Concentration, mg/kg
Li	142	B	500
Na	57,000	Al	2
K	10,000	Fe	230
Rb	58	Mn	680
Cs	11	Si	250
Mg	84	Cu	1
Ca	23,000	Pb	60
Sr	418	Zn	290
Ba	150	Sn	∿1
		Cd	1.5
P	9		
As	10	Sulfate	40
Sb	2	Au	0.1
		Pt	0.06
Co, Ni, Ti,		Ag	0.6
V, Zr,	<1		

Table 2. Approximate scaling rates and compositions of scales formed at the
Salton Sea Geothermal Field.

Temperature, °C	Scaling rate, mm/day (mil/h)	Character and compounds identified
220-200	0.03-0.06 (0.05-0.10)	PbS, ZnS, Cu_2S, $CuFeS_2$, Ag, in Fe-rich amorphous silica matrix (Ref. 14)
		Above + FeS_2, $CuAgS$, $FeAsS$, $(Cu,Ag,Zn,Fe)_{12}(Sb,As)_4S_{13}$, Cu_5FeS_4, Cu_9S_5 (Ref. 15)
180-110	0.06-0.6 (0.1-1.0)	Amorphous silica matrix with some Fe and sulfide compounds
105-85	0.6-3 (1-5)	Amorphous silica matrix with Fe compounds and entrained brine solids

Table 3. Elemental analysis of scales formed on flat coupons by untreated brine at 125°C (Magmamax No. 1 brine; 4.0 mol/l chloride; 113 h exposure; 0.3-0.6 mm scale thickness)

Element	Element concentration, wt. %		
	TFE Teflon Coupon	Hastelloy C-276 Coupon	Mild steel (AISI 1009) Coupon
Si as SiO_2	83	81	66
Na	n.d.	0.5	0.6
K	0.8	1.0	0.7
Ca	0.45	0.45	0.75
B	n.d.	0.06	0.6
Al	n.d.	n.d.	1.9
S	0.3	0.44	1.1
As	0.03	<0.01	0.53
Sb	<0.02	0.02	2.8
Fe	1.1	1.0	2.3
Cu	0.59	0.31	6.0
Pb	0.21	1.6	0.91

n.d. = not determined

Table 4. Types and examples of organic compounds that inhibit the precipitation of silica from geothermal brine.

Trade Name	Manufacturer	Chemical Name[a]
Hydroxyethylcelluloses (HEC)		
Natrosol 250LR	Hercules	HEC, M.W. = 85,000
Polymer JR-125	Union Carbide	Amine-substituted HEC
Polyoxyethylene Polymers:		
Carbowax 14,000	Union Carbide	Polyoxyethylene, M.W. = 14,000
Ethoxylated Amines:		
Ethomeen 18/25	Armak	Polyoxyethylene(15) octadecyl-amine
Ethomeen 18/60	Armak	Polyoxyethylene(50) octadecyl-amine
Ethomeen C/25	Armak	Polyoxyethylene(15) cocoamine
Quaternary Ammonium Compounds:		
Ethoquad 18/25	Armak	Methylpolyoxyethylene(15) octadecylammonium chloride
Hyamine 1622	Rohm & Haas	Di-isobutylphenoxyethoxyethyl-dimethylbenzylammonium chloride
Q-C-50	Tomah	Methylpolyoxyethylene(50) cocoammonium chloride
Other Ethoxylated Compounds:		
Pluronic F38	BASF-Wyandotte	Polyoxyethylene/polyoxypropylene block copolymer, M.W. = 5000
Conco NI-125	Continental	Polyoxyethylene(200) nonyl phenol
Lipal 200C	PVO Int'l	Polyoxyethylene(200) ricinoleic acid triglyceride
Jeffox FF-200	Jefferson	Polyoxyethylene/polyoxypropylene random copolymer, M.W. = 10,000
Miscellaneous Compounds:		
Corcat P-200	Cordova	Polyethylene imine, M.W. - 20,000
XD-8779.00	Dow Chemical	Polyethyloxazaline, M.W. = 60,000
PAE·HCl	Dynapol	Poly(aminoethylene, HCl salt) M.W. = 120,000

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[a]Number in parentheses denotes the number of molecules of ethylene oxide per molecule of additive.
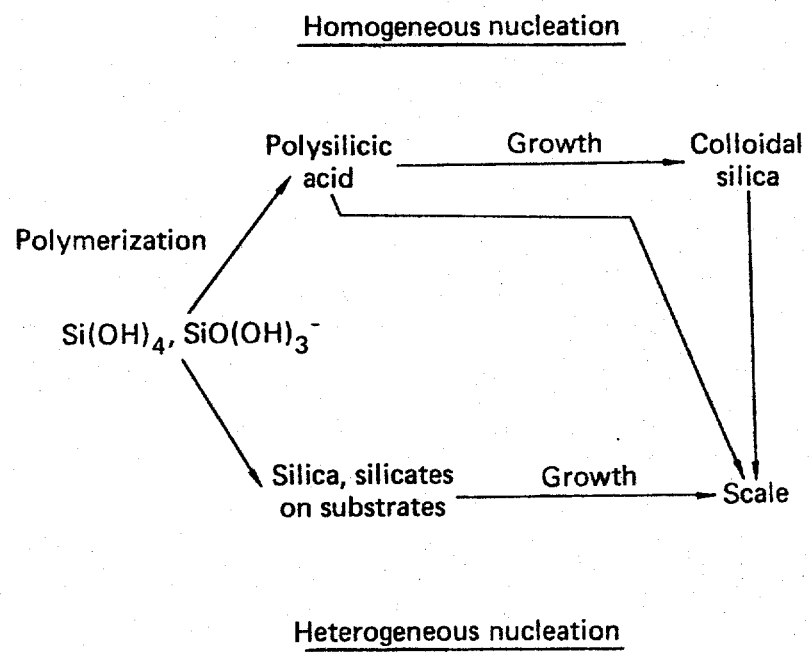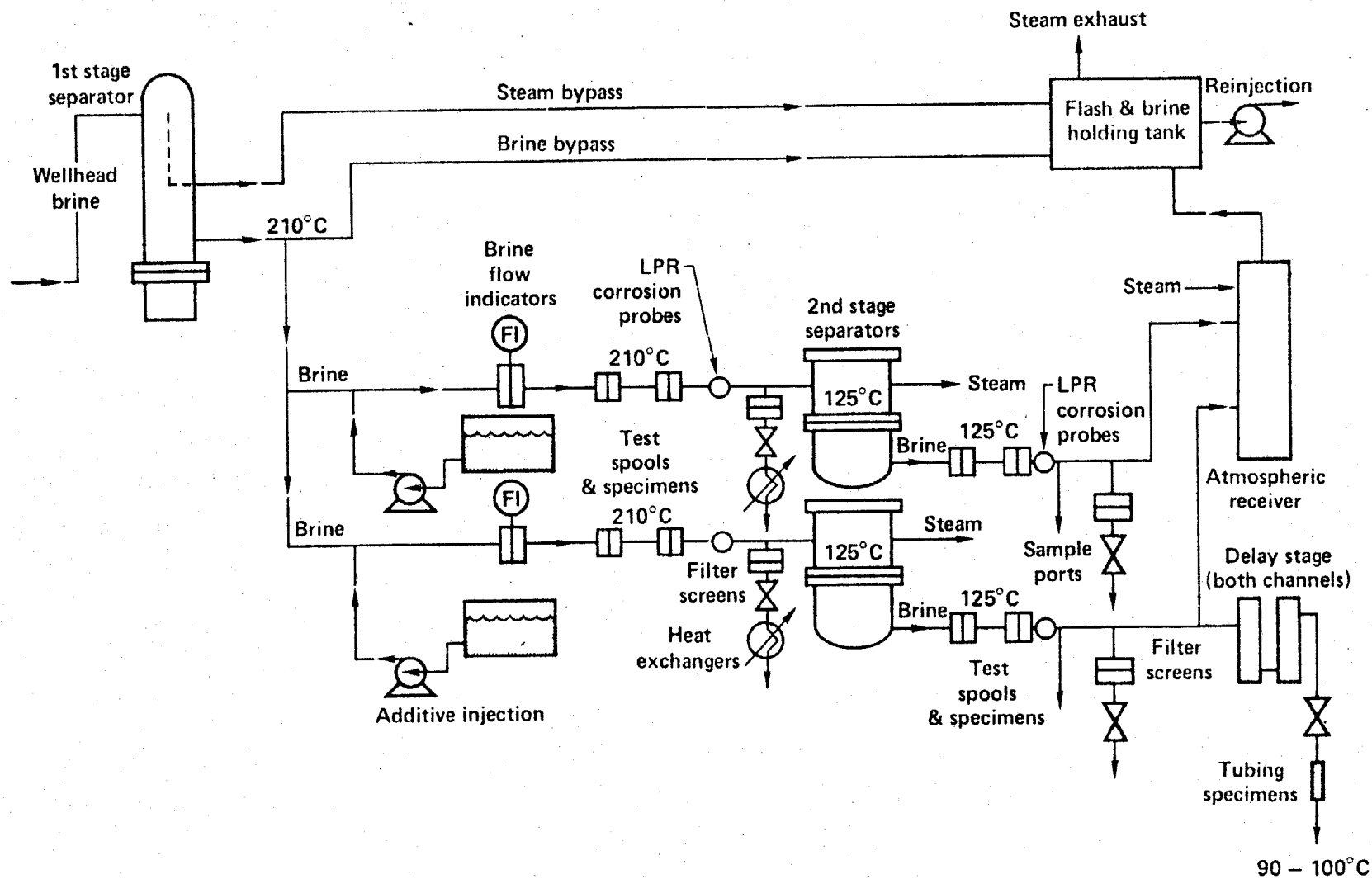
Table 5. Effect of additives on scaling rates of geothermal brine
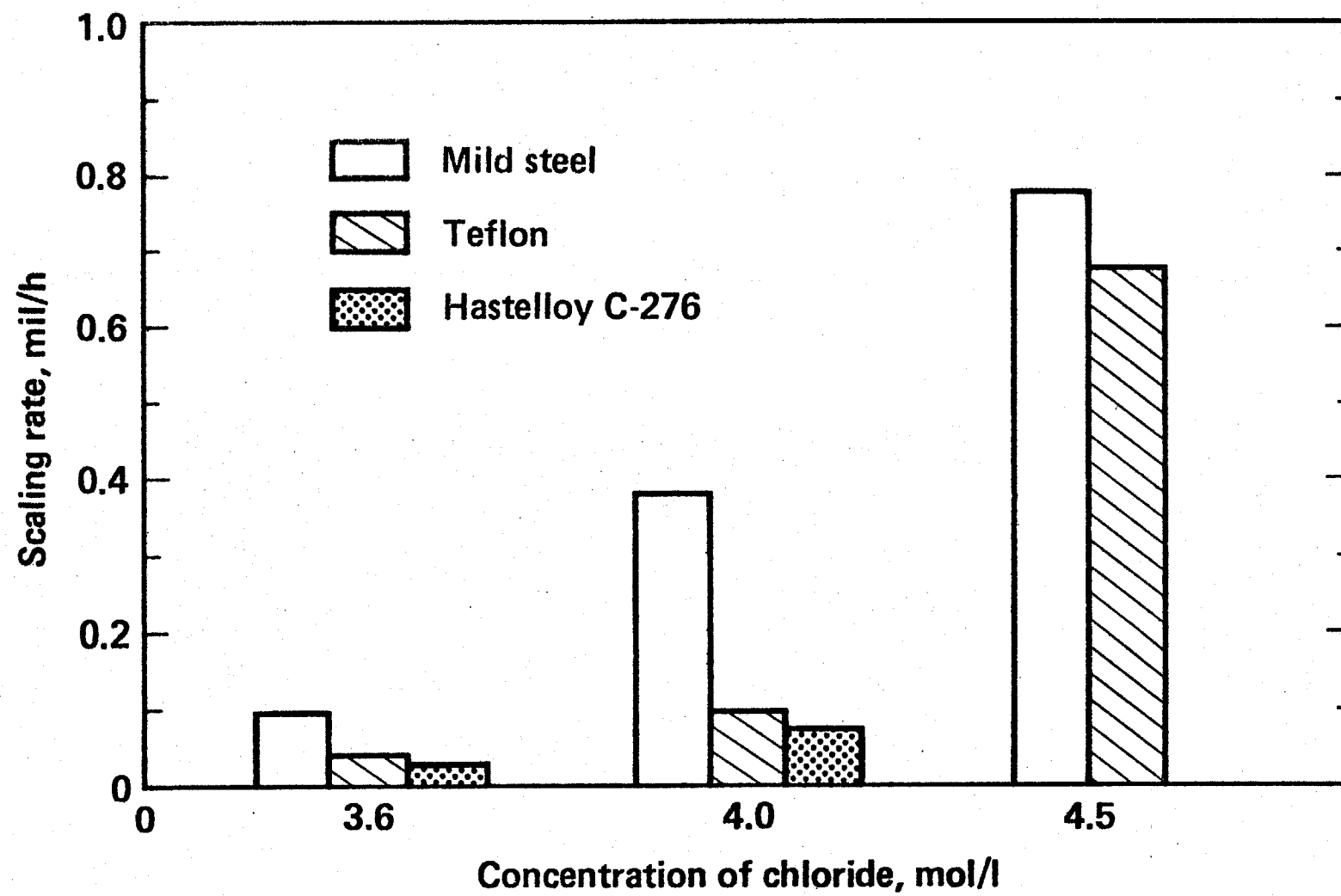(Magmamax No. 1 brine, 4.0-4.5 mol/l chloride)

Additive	Time of Exposure h	Scaling Rate, mil/h						
		Coupon, 210°C			Coupon, 125°C			Tubing, 90°C
		Mild Steel	Hastelloy	Teflon	Mild Steel	Hastelloy	Teflon	Mild Steel
None, Control	69	0.10	0.03	0.06	0.78	-	0.68	4.8[a]
Ethoquad 18/25 (25 ppm)	69	0.41	0.30	0.14	0.67	0.42	0.51	2.7[a]
Ethoquad 18/25 (20 ppm) + Dequest 2060 (5 ppm)	66	0.15	0.08	0.10	0.44	0.53	0.53	0.9[b]

[a] 4.0 mol/l chloride; 13 h exposure.

[b] 4.5 mol/l chloride; 25 h exposure.

Homogeneous nucleation

Polysilicic acid — Growth → Colloidal silica

Polymerization

$Si(OH)_4$, $SiO(OH)_3^-$

Silica, silicates on substrates — Growth → Scale

Heterogeneous nucleation

1st stage separator

Wellhead brine

Steam exhaust

Steam bypass

Brine bypass

Flash & brine holding tank

Reinjection

210°C

Brine flow indicators

LPR corrosion probes

2nd stage separators

Steam

FI

210°C

125°C

Steam

LPR corrosion probes

Brine

Test spools & specimens

Brine 125°C

Atmospheric receiver

Sample ports

Additive injection

FI

210°C

Filter screens

Heat exchangers

125°C

Steam

Brine 125°C

Test spools & specimens

Delay stage (both channels)
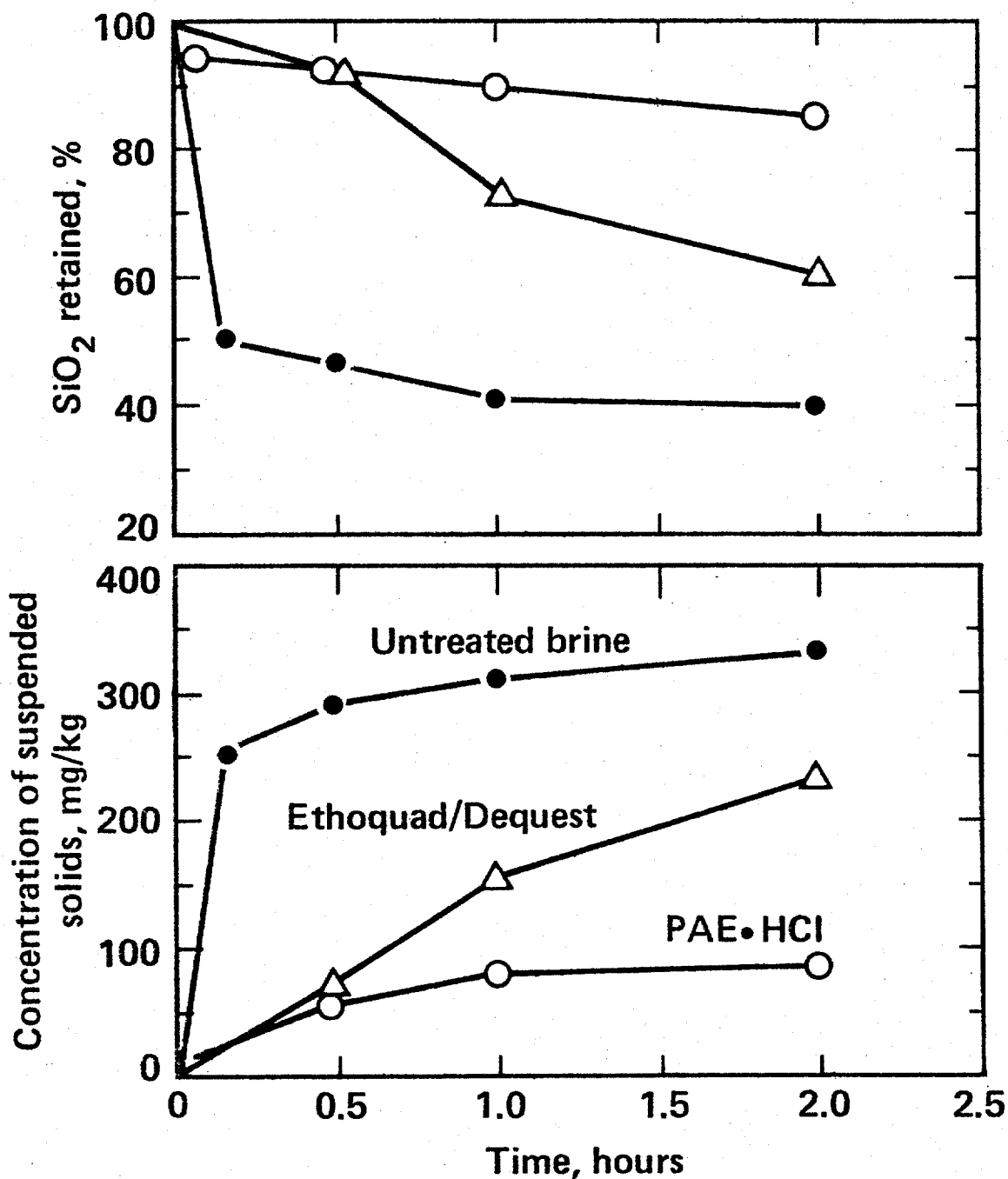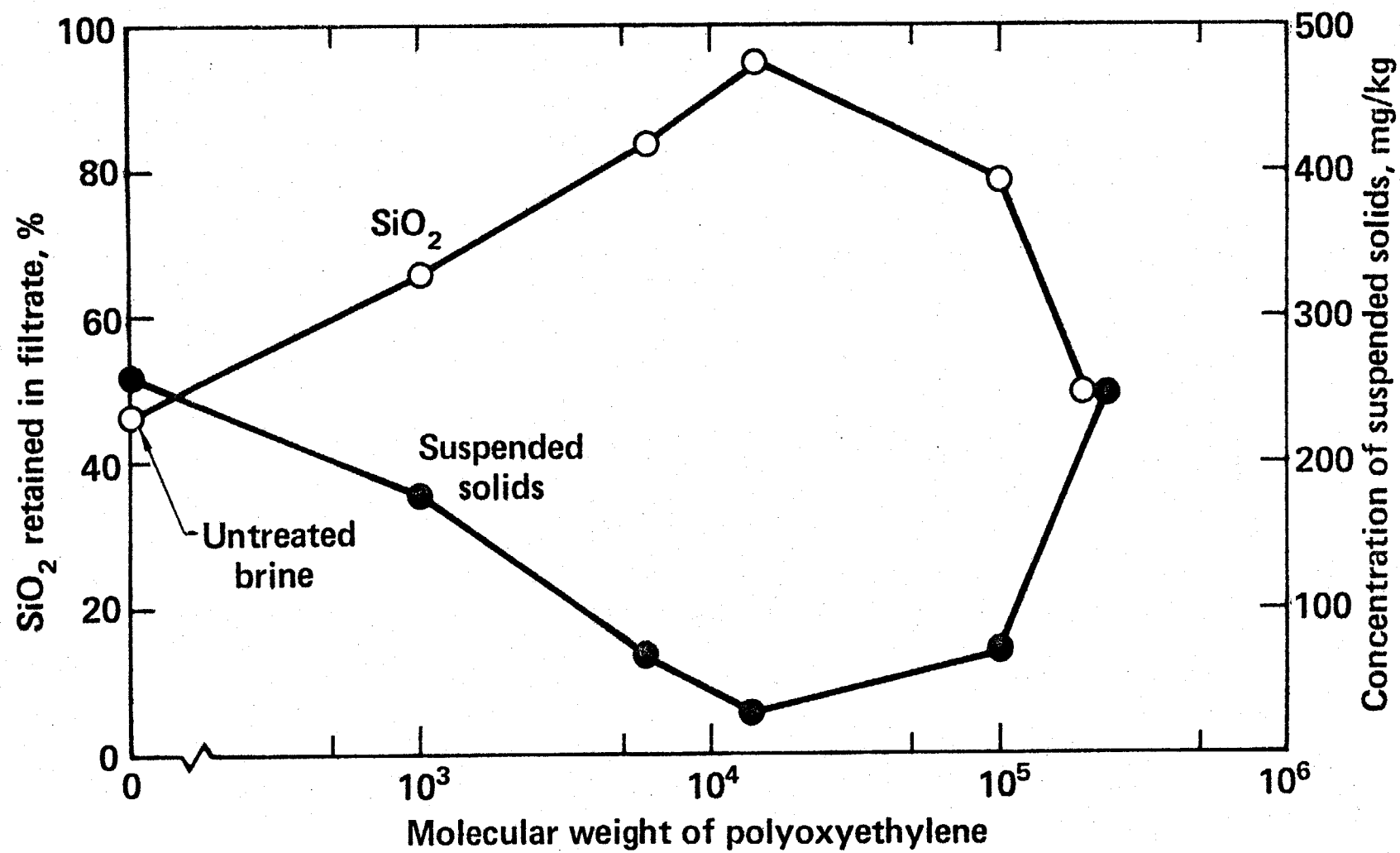
Filter screens

Tubing specimens

90 – 100°C

INHIBITION OF PRECIPITATION OF SOLIDS AND SILICA FROM GEOTHERMAL BRINE BY ORGANIC ADDITIVES

20 ppm Additive; Incubation at 90°C

FIGURE CAPTIONS

Figure 1. Pathways for the formation of scale from monomeric silica (adapted from Ref. 20).

Figure 2. Schematic diagram of the Lawrence Livermore Laboratory brine-treatment Test system.

Figure 3. Effect of brine salinity on scaling rates at 125°C (Magmamax No. 1 brine, concentration of SiO_2 ~500 mg/kg).

Figure 4. Inhibition of the precipitation of solids and silica from geothermal brine by organic additives (Magmamax No. 1 brine, 4.5 mol/l chloride; 20 ppm additive, incubation at 90°C).

Figure 5. Inhibition of the precipitation of silica from geothermal brine by polyoxyethylene compounds (Magmamax No. 1 brine, 3.6 mol/l chloride; 20 ppm additive, incubation at 90°C).